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Pesticide pollution in argentine drinking water: A call to ensure safe access

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ABSTRACT

The application of pesticides in Argentina has been on the rise since 2000. However, the monitoring of pesticides in drinking water lacks regular updates. This research study analysed 53 pesticides and degradation products to evaluate their presence in drinking water. The most frequently detected pesticides in drinking water were atrazine, metolachlor, imidacloprid, hydroxyatrazine, imazethapyr and 2.4D. During the sample collection period, 25% of the soil was planted with winter crops, while just under 50% was allocated to summer crops, especially corn and soybeans. The correlation between the pesticides used in these crops and those found in drinking water was significant/notable. As a matter of fact, the individual concentration of pesticides in drinking water [25] exceeded the European limit in 8.7% and 17.6% of the samples collected from public and private water supplies, respectively, while the cumulative concentration of pesticides in drinking water exceeded the limit in 4.3% and 13.9% of the samples from public and private supplies, respectively. Based on these findings, we recommend/propose the inclusion of pesticides within the regulatory framework that governs the quality control of drinking water to guarantee the protection of public health and progressively reduce the use of pesticides in the Argentine agricultural system. Adopting these measures will contribute to ensuring the safety and sustainability of drinking water sources for the population.

Introduction

Water is essential for human survival, production of food, energy, and socioeconomic development (European Union 2023). In 2010, the United Nations General Assembly recognized the human right to safe, sufficient, acceptable, affordable, and physically accessible water for domestic use. Groundwater is the main source in many regions of the world (Carrard et al., 2019; Guppy et al., 2018; Hanak et al., 2011) and its composition is influenced by geology, land management, environmental conditions, and well characteristics (Leite et al., 2018). A multivariate statistical analysis has shown that the proper location of a well within a farm is the main factor that contributes to preserving groundwater quality, thereby reducing its susceptibility to external influences related to anthropogenic uses, such as agriculture or livestock (Urseler et al., 2022).

The risk of drinking water contamination is linked to soil vulnerability, pesticide application frequency, dosage, and timing (Caprile et al., 2017). Scientific literature furnishes information on soil-pesticide relationships to understand which environments are more vulnerable to the vertical transport of specific pesticides (Shomar et al., 2006; Székács et al., 2015; Munira et al., 2018; Lutri et al., 2020; Gonzalo Mayoral et al., 2021; Gonzalo Mayoral et al., 2022). Leveraging this information could prevent or restrict the application of pesticides in vulnerable environments. The agricultural and livestock practices have led to groundwater contamination in several countries across the globe, mainly due to the use of fertilizers, pesticides, and animal manure (Munira et al., 2018; Lutri et al., 2020; Gilliom, 2007; Gonzalez et al., 2012; Silva et al., 2012; Lupi et al., 2015; Li et al., 2016; Montoya et al., 2019; Blarasin et al., 2020; Mas et al., 2020; Costa et al., 2020; Baran et al., 2022). The intensification of agricultural production must be accompanied by effective land planning programs (MINISTRY OF HEALTH PRESIDENCY OF THE NATION, 2007).

In the Netherlands, 15 of the 24 newly/recently authorized pesticides that are not yet included in routine monitoring programs were detected, including seven other pesticides at concentrations above the water quality standard. The infiltration of pesticides, authorized within the last 10 years, into drinking water sources underscores the importance of updating routine monitoring methods (Sjerps et al., 2019). Pesticide traces in drinking water can potentially affect human health, depending on the quantity/toxicity of the pesticides and the frequency/duration of human exposure to contaminated drinking water. Hazardous pesticides have also been identified, most of them classified

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as cholinesterase inhibitors (El-Nahhal and El-Nahhal, 2021). Exposure to low-dose pesticide mixtures can have prolonged adverse health effects, some of which are related to the rise of chronic degenerative diseases, impaired neurodevelopment, and cancer (Miranda et al., 2023; Nicolella and de Assis, 2022; Gonsioroski et al., 2020). In addition, the health implications caused by certain pesticide mixtures may diverge from the effects of their individual components, raising health concerns (Hernández et al., 2013). A study conducted on the populations of eight small Argentine rural towns revealed a higher incidence of cancer among those living in close proximity to pesticide applications (Verzeñassi et al., 2023). Verzeñassi et al. (2023) argued that some cancer types have been linked to specific pesticides, e.g., non-Hodgkin's lymphoma to glyphosate (Weisenburger, 2021) or lung cancer to 2-4-D (Kaur et al., 2021). The constant exposure to pesticides through the ingestion of contaminated water has been associated with hormonal imbalance, reproductive problems, carcinogenic effects, and reduced intelligence, particularly in children in the stage of body development (Yadav et al., 2015).

Many countries establish maximum residue levels (MRLs) of pesticides in drinking water to protect human health. A recent study indicated that some of the MRLs of pesticides surpass safe thresholds, undermining the goal of safeguarding public health (Li and Jennings, 2017). The standard values for the most commonly regulated pesticides vary by seven, eight, or nine orders of magnitude, denoting a lack of consensus regarding the maximum permissible values worldwide (Li and Jennings, 2017). The European Union has the most stringent standards, with the lowest concentration threshold set at 0.1 $\mu g\ L^{-1}$ for pesticides (CEU, 1998). In 2023, European regulations were updated to include revised safety standards, emerging substances such as microplastics and endocrine disruptors, and new chemical products that require control. The new regulations ensure the application of one of the highest global standards for drinking water, aligning with the zero-pollution ambition outlined in the European Green Deal (European Commission, 2016).

The agro-industrial model consolidated in the Southern Cone countries (Brazil, Argentina, Paraguay, Uruguay, and Bolivia) in the late 20th century. During the 2018/2019 harvest(?) season in Argentina, soybeans and corn collectively accounted for 66.7% of the total agricultural area, with a volume of pesticides usage reaching 373,820,837 kg or L, approximately averaging 8.3 kg or L ha^{-1}, according to data compiled by the Chamber of Agricultural Health and Fertilizers (CASAFE, 2018). The Argentine Government relies on figures from business chambers to report on the use of pesticides as there are no official data on the quantities administered, nor are there any systematic environmental or health surveys on their effects (Gárgano, 2022).

Argentina has committed to the United Nations Sustainable Development Goals. Although its regulations on the use of pesticides align with those of leading agricultural countries, the focus is limited to acute toxicity and fails to consider possible chronic effects, an aspect that is currently under investigation and debate in various countries (Montoya et al., 2023). Additionally, the National Drugs, Food, and Medical Devices Administration ANMAT (2012), in its chapter XII on drinking water quality control, proposes a list of pesticides and concentration levels that must be measured. However, except for one herbicide, 2,4-D, this list is outdated. As a result, the presence of pesticides in the water consumed by the population throughout the country remains unnoticed (Gárgano, 2022).

In this context, conflicts linked to water contamination due to pesticide use emerge. The communities of the Pampas region have expressed concerns about the quality of the water they drink on a daily basis. The Pesticide Analysis Laboratory of the Agricultural Experimental Station of the National Institute of Agricultural Technology of Balcarce (EEA INTA Balcarce) began receiving and analysing samples of water for human consumption in the early 2010s, and this demand has steadily increased over time. In 2018, the Federal Court issued a first ruling at the epicentre of the country's agricultural activity. The Court held state officials criminally responsible and implemented precautionary measures, considering both water contamination and documented health effects attributed to pesticides. It further summoned researchers and official organizations to contribute to the scientific analysis of evidence, marking an unprecedented event in Argentina's justice system (Gárgano, 2022).

The objective of this research study is to provide information on the presence and concentration levels of pesticides and degradation products in water from underground sources intended for human consumption to substantiate the need to adopt national regulations concerning pesticide contents in drinking water. To the best of our knowledge, this is the first scientific study to identify the predominant pesticides, among the 53 tested pesticides and degradation products, and their respective concentration levels found in groundwater used to supply drinking water in Argentina.

Materials and methods

(a) Hydrological characterization of the pampas plain (Argentina)

The Pampas plain covers an area of approximately 500,000 km^2, with elevations below 200 m above sea level. This plain predominantly consists of a silty (loessic) sedimentary deposit of Quaternary age, which overlays various sedimentary basins of different ages and geological origins. The landscape is characterized by low topographic slopes, low drainage density, and the presence of relatively permeable materials on the surface (Sala et al., 1983).

Near the mountain fronts, alluvial cones are observed, forming a classic piedmont where the drainage exhibits typical characteristics of such environments. These streams tend to diminish or lack tributaries as they move away from the mountain front, often transforming into gently concave areas where water is temporarily retained in depressions (Sala et al., 1985).

The low slope in the Pampas plain reduces the regional surface runoff velocity, prolonging the contact times between water and the land surface. This fosters increased infiltration and evapotranspiration. Noteworthy in this region are the significant roles of vertical transport processes and surface storage (Kruse and Zimmermann, 2002).

b) Water sample collection

The Pesticide Analysis Laboratory of the EEA INTA Balcarce was contacted by neighbouring communities, municipalities and organized agri farmers to inquire about the presence of pesticides in water intended for human consumption.

Groundwater samples were collected between 2019 and 2022. The sampled groundwater had depths ranging from a minimum of 17 meters to over 50 meters.

Samples (n=154) were collected after pumping water to clean standing water in pipelines. The sample collection required propylene bottles, which were rinsed three times with the pumped water before sampling. The water samples were stored at -20°C prior to transportation to the laboratory, maintaining the cold chain. Fig. 1 illustrates the territorial distribution of samples during the four-year period, and Table 1 provides the geographic coordinates of the sampling sites. The selection of pesticides for analysis was based on usage frequency, as recommended by agronomy experts who advise farmers in the southeast as well as agri input companies in the area.

(c) Laboratory analysis method

Water samples were thawed overnight at 4°C and filtered through a 0.45 μm nylon membrane to separate water from suspended particles. The pesticides and degradation products analysed (e.g., AMPA, hydroxy-atrazine, among others) are listed in Table 2 and were determined using ultra-high performance liquid chromatography coupled with triple

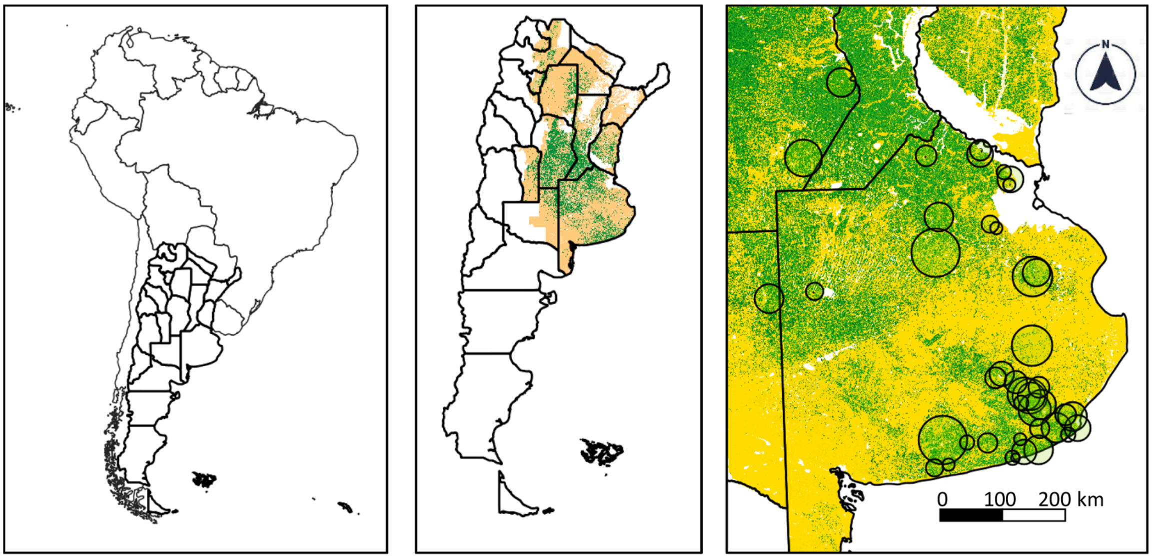

Fig 1. Locations of drinking water samples tested.

quadrupole tandem mass spectrometry (UHPLC-MS/MS), following the methods described by De Gerónimo et al. (2014) and Aparicio et al. (2013). The methods were validated, considering parameters such as analytical recoveries, detection limits (DL), quantification limits (QL), precision, linearity, and matrix effect (De Gerónimo et al., 2014).

Chromatographic separation was conducted using an Acquity UPLC BEH C18 column (1.7 µm, 100 × 2.1 mm, Waters) equipped with an Acquity VanGuard BEH C18 guard column (1.7 µm, 5 × 2.1 mm, Waters). The mobile phase consisted of water/methanol (95:5) modified with 0.1 mM ammonium acetate and 0.01% of formic acid (Phase A), and methanol modified with 0.1 mM ammonium acetate and 0.01% of formic acid (Phase B), using gradients from 10% to 100% of Phase B. Nitrogen from a generator was employed as drying and nebulizing gas, while 99.99% of argon with a pressure of 6.3×10^{-3} mbar in the T-Wave cell served as collision gas. All data were processed using Masslynx™ 4.1 (Waters Corporation ®). (De Gerónimo et al., 2014; Aparicio et al., 2013)

(d) Data processing and calculations

The concentration levels of pesticides and degradation products were classified into two groups based on the drinking water source: ***(a)*** public supply and ***(b)*** private supply.

In case ***(a)***, groundwater wells were constructed to supply drinking water to cities, and the water quality is monitored either by state authorities or water supply companies. In case ***(b)***, wells were dug by families living in rural areas such as country houses or small villages, and the responsibility for water quality control lies with the individual user.

Initially, the frequency of pesticides and degradation products found in each water sample was analysed through histograms. The total sum of molecules was represented on a map along with their respective locations. If multiple samples were obtained from a city, small village, or rural house, the one exhibiting the highest total molecule count was selected to analyse the less satisfactory results in each area. Subsequently, only the data exceeding the quantification limit (QL) of the analytical method used were considered. Based on these results, we estimated the concentration range of each pesticide in the samples from both groups. We specifically analysed the pesticides and degradation products that surpassed the concentration thresholds established by the Council of the European Union (CEU), both at the individual and group levels (CEU, 1998). The concentration was stated in µg L^{-1}.

(e) Preparation of crop maps linked to the presence and concentration of pesticides in drinking water

The information regarding pesticides and degradation products in drinking water was analysed in conjunction with the distribution of winter crops (in 2020) and summer crops (in 2020-2021). The crops' surface data was obtained from the GeoINTA database (GeoINTA, 2023). We defined an area of influence around the analysed sites and cropped the raster file downloaded from GeoINTA using this defined area. Subsequently, the r.report plugin from the QGIS program (QGIS.org, 2023) was applied to obtain the statistics of the clipped raster layer. This process allowed us to determine the areas where winter and summer crops were cultivated.

Results and analysis

(a) Presence of pesticides in drinking water

The research study revealed a widespread presence of pesticides and degradation products in the drinking water of the Pampas region. A high percentage of pesticides and degradation products, 69% in public supply (n=46, Fig. 2a) and 89% in private supply (n=108, Fig. 2b), were encountered in at least one sample. This finding aligns with the observations made by El-Nahhal and El-Nahhal (2021), who detected approximately 113 pesticides residue in drinking water samples from 31 countries worldwide, highlighting the global nature of the problem.

Although local water supply companies monitor the quality of drinking water to detect pesticides and degradation products in compliance with Argentine regulations, the population is exposed to chemical products that are not monitored because of the current standards' obsolescence. Proactive monitoring, including newly authorized pesticides, can help identify potential risks (Dolan et al., 2013; Dolan et al., 2014). Several factors contribute to the potential risks associated with pesticides in the production of drinking water, ranging from large-scale agricultural practices (e.g., monocultures or perennial crops) to the varied uses of active ingredients (Sjerps et al., 2019).

The most frequently detected pesticides in both public supply (atrazine, imidacloprid, hydroxy-atrazine, imazethapyr, and 2.4D; Fig. 2a) and private supply (atrazine, metolachlor, hydroxy-atrazine, imidacloprid; Fig. 2b) were practically the same. Agricultural management practices expose both urban and rural residents to the same pesticides, although those individuals consuming water from private supply experience higher levels of exposure.

Table 1
Geocoordinates of the sampling sites.

Supply	Geocoordinates	
	x	y
Public	-58,504926	-36,836311
	-61,130322	-34,122468
	-59,558363	-34,059974
	-59,387875	-33,908512
	-59,497917	-33,799930
	-59,132154	-35,272698
	-59,263845	-38,005541
	-64,346115	-33,121593
	-63,566199	-36,055195
	-58,716260	-38,554354
	-62,733179	-35,967475
	-59,274717	-35,006910
	-57,561924	-37,998794
	-61,351509	-37,984831
	-60,889500	-38,330700
	-60,452502	-38,722655
	-61,260344	-37,243001
	-60,554184	-33,899076
	-58,959126	-35,671804
	-58,577561	-35,873136
	-58,496414	-35,768750
Private	-60,242331	-38,322970
	-60,378246	-35,401627
	-58,505340	-36,845209
	-58,513295	-35,760143
	-62,840198	-33,882201
	-58,640629	-37,602432
	-58,435393	-37,833791
	-58,712005	-38,305210
	-58,003023	-38,115924
	-58,300954	-37,760933
	-58,347614	-38,463424
	-57,683616	-37,930535
	-63,584936	-36,056731
	-62,105785	-32,720571
	-60,306043	-34,843418
	-58,447120	-35,693954
	-59,529491	-33,853450
	-59,527321	-33,796398
	-58,960957	-34,251049
	-59,338273	-34,946645
	-59,076621	-34,144545
	-60,539635	-33,891781
	-62,703824	-35,970208
	-59,220550	-35,009254
	-58,985738	-34,328858
	-57,576567	-38,107760
	-58,628778	-38,498467
	-59,091261	-37,288855
	-58,810560	-37,416436
	-59,203454	-37,352566
	-58,356603	-37,483111
	-57,824095	-37,904556
	-58,332636	-38,132377
	-59,354192	-38,360304
	-59,331398	-38,449891
	-60,418470	-38,755598
	-59,754026	-38,364733
	-60,128182	-38,705757
	-58,627768	-38,561374
	-58,797248	-38,593869
	-58,783990	-38,587227
	-58,855892	-38,589480
	-57,756697	-38,218324
	-58,691250	-37,734043
	-58,507577	-37,622913
	-58,535726	-37,626011

The degradation rate of pesticides decreases as they penetrate deeper into the soil due to reduced microbial population and organic matter (Rasool and Thakur, 2022). Pesticides tend to persist longer in drinking water than in soil. Therefore, adopting these two measures is essential: (i) prevent transport of pesticides through the soil profile by considering their "space-time combination" and the edaphoclimatic conditions that favour their vertical transport, and (ii) maintain a distance between areas where pesticides are applied and areas where water is extracted for consumption. Given the low slope of the region, horizontal movement of groundwater can be considered negligible. Thus, relocating pesticide applications away from the pumping zone reduces the probability of pesticides being available for vertical transport through the soil profile and reaching drinking water.

The number of pesticides detected per sample ranged from 1 to 22 in public supply and from 0 to 31 in private supply out of a total of 53 substances analysed. The geographical distribution of these results is displayed in Fig 3a and b. Human exposure to multiple pesticides is a growing scientific concern as the combined toxicological effects of two or more components of a pesticide mixture at low doses have been poorly studied to date (Hernández et al., 2013). These findings suggest that, in the near future, regulations will need to acknowledge the adverse health effects of pesticide interactions to provide acomprehensive approach to safeguarding human health (Hernández et al., 2013).

(b) Concentration of pesticides in drinking water

In some cases, the concentration of pesticides exceeded the individual threshold of 0.1 μg L^{-1} set by the CEU in 1998. In public supply, 4 pesticides and 1 degradation product exceeded the threshold, while in private supply, 19 pesticides and 1 degradation product exceeded the threshold (see Table 3).

The higher concentration of pesticides above the individual European threshold in well water samples could be attributed to the depth of water extraction (CEU, 1998). Generally, the extraction depth of public supply (> 35 m) is greater than that of private supply (17 to 20 m). In the Netherlands, concentrations greater than 0.1 μg L^{-1} were found in 27% to 55% of drinking water monitoring wells at depths between 1 and 7 m. However, this range decreases in wells exceeding 20 m in depth (where pesticides are used) (Schipper et al., 2008).

Pesticide loss through flow in macropores usually amount to less than 1% of the applied quantity but can reach up to 5% in some cases (Jarvis, 2007). Despite these percentages suggesting a limited physical process, Jarvis (2007) examined the EU drinking water standard (0.1 μg L^{-1}), a dose of 0.2 kg ha^{-1}, and an annual recharge of 200 mm. He found that the maximum permissible leaching loss only accounted for 0.1% of the quantity applied.

Pesticides and degradation products with a maximum concentration greater than 10 μg L^{-1} in drinking water were meticulously examined. Glyphosate, classified as "probably carcinogenic to humans" (Group 2A) by the World Health Organization ((WHO, 2015), and AMPA, a residue of toxicological interest, both warrant evaluation in drinking water considering their presence in the current results.

The herbicide 2,4-D is one of the most commonly regulated pesticides in drinking water, with 180 MRLs, including 59 US MRLs and 121 worldwide MRLs (Li and Jennings, 2017). In Argentina, the MRL for 2, 4-D is 100 μg L^{-1} (ANMAT, 2012), which falls within the uncertainty limits associated with the potential risk to human health derived from MRLs set for 2,4-D in drinking water (30, 470 μg L^{-1}) (Li and Jennings, 2017). The World Health Organization has classified 2,4-D as ”possibly carcinogenic to humans” (Group 2B) based on strong evidence of its capacity/potential to induce oxidative stress and moderate evidence suggesting immunosuppression in humans, as supported by *in vivo* and *in vitro* studies (WHO, 2015).

Europe set the MRL for pesticide molecules in water samples at 0.5 μg L^{-1} (CEU, 1998). This threshold serves to assess exposure to multiple pesticides, and this research study shows that 2 public supply water samples and 15 private supply water samples exceeded it (Fig. 4a, b). Herbicides constitute the group of pesticides with the highest presence in water intended for human consumption.

Table 2
Pesticides MS/MS conditions.

Pesticides	Polarity	Q transition	Cone (V)	Col. Ener. (eV)	q transition	Col. Ener. (eV)	LOD	LOQ
2,4-D	ESI-	218 > 160.8	19	18	218 > 124.8	26	0,005	0,015
2,4-DB	ESI-	246.9 > 160.8	12	12	248.9 > 162.8	12	0,010	0,040
Acetochlor	ESI+	269.9 > 147.9	10	20	269.9 > 224	8	0,003	0,008
Alachlor	ESI+	265.9 > 173.9	11	15	265.9 > 220	5	0,003	0,008
Aldicarb	ESI+	212.9 > 115.8	23	13	212.9 > 88.9	20	0,004	0,013
Allethrin	ESI+	303 > 134.9	15	13	303 > 92.8	13	0,001	0,004
Ametrine	ESI+	228 > 185.9	20	20	228 > 95.9	28	0,001	0,003
AMPA-FMOC $^{(*)}$	ESI+	334 > 179.1	25	25	334 > 112	15	0,08	0,15
Atrazine	ESI+	215.9 > 173.9	28	18	215.9 > 95.9	23	0,001	0,004
Atz-desethyl $^{(*)}$	ESI+	187.8 > 145.8	25	18	187.8 > 103.8	25	0,0004	0,002
Atz-desisopropyl $^{(*)}$	ESI+	173.8 > 95.8	25	18	173.8 > 103.7	13	0,002	0,006
Atz-OH $^{(*)}$	ESI+	198 > 156	28	18	198 > 85.9	23	0,003	0,009
Carbaryl	ESI+	201.9 > 144.9	18	13	201.9 > 126.9	23	0,003	0,009
Carbofuran	ESI+	222 > 164.9	30	13	222 > 122.9	22	0,002	0,006
Ethyl Chlorimuron	ESI+	414.9 > 185.9	23	20	414.9 > 212.9	18	0,003	0,007
Chlorpyrifos	ESI+	349.7 > 96.8	25	30	351.7 > 96.8	32	0,003	0,011
Chlorpyrifos-Methyl	ESI+	323.7 > 124.8	20	25	321.7 > 124.8	25	0,002	0,005
DEET	ESI+	191.9 > 118.9	27	18	191.9 > 90.9	30	0,002	0,005
Diazinon	ESI+	305 > 168.9	28	20	305 > 152.9	23	0,001	0,004
Dicamba	ESI-	218.8 > 174.8	10	8	220.8 > 176.8	8	0,030	0,090
Dichlorvos	ESI+	220.8 > 108.8	23	18	222.8 > 108.8	18	0,002	0,006
Diclosulam	ESI+	405.9 > 160.9	34	25	407.9 > 162.9	25	0,002	0,006
Dimethoate	ESI+	229.8 > 198.9	28	10	229.8 > 124.8	23	0,001	0,003
Epoxiconazole	ESI+	329.9 > 120.9	25	23	329.9 > 122.9	23	0,001	0,002
Fipronil	ESI-	436.8 > 331.9	23	15	434.8 > 329.9	15	0,001	0,003
Flumioxazin	ESI+	355.2 > 327	38	22	355.2 > 298.9	28	0,002	0,006
Flurochloridone	ESI+	311.8 > 291.9	40	21	313.8 > 293.9	21	0,002	0,006
Fomesafen	ESI+	456.1 > 343.8	22	15	456.1 > 223	31	0,003	0,009
Glyphosate-FMOC	ESI+	392 > 88	25	20	392 > 179.1	25	0,05	0,10
Glufosinate-FMOC	ESI+	404.1 > 136	25	25	404.1 > 207.9	10	0,05	0,10
Imazapic	ESI+	276 > 162.9	33	28	276 > 231.1	20	0,001	0,004
Imazapyr	ESI+	261.9 > 217	25	20	261.9 > 148.8	25	0,001	0,004
Imazaquin	ESI+	312 > 199	28	28	312 > 267	20	0,0003	0,0010
Imazethapyr	ESI+	290 > 176.9	30	27	290 > 245.1	20	0,001	0,004
Imidacloprid	ESI+	255.9 > 175	22	20	255.9 > 209	15	0,003	0,008
Kresoxim Methyl	ESI+	314 > 206	15	8	314 > 115.9	15	0,001	0,002
Malathion	ESI+	330.9 > 126.9	18	13	330.9 > 98.9	23	0,002	0,004
Metalaxyl	ESI+	280 > 220	23	15	280 > 192	18	0,001	0,004
Metconazole	ESI+	320 > 70	35	25	320 > 124.8	33	0,002	0,006
Methobromuron	ESI+	258.8 > 169.8	20	20	260.8 > 169.8	20	0,000	0,000
Metolachlor	ESI+	284 > 252	25	15	284 > 176	25	0,001	0,004
Methomyl	ESI+	162.9 > 88.1	16	10	162.9 > 106.1	10	0,002	0,006
Metribuzin	ESI+	215 > 187	23	20	215 > 83.9	20	0,000	0,001
Metsulfuron Methyl	ESI+	381.9 > 166.8	18	18	381.9 > 198.8	22	0,002	0,006
Methyl Parathion	ESI+	263.9 > 231.8			263.9 > 124.8		0,002	0,006
Pendimentalin	ESI+	282 > 212	15	10	282 > 194	20	0,006	0,019
Picloran	ESI-	240.8 > 196.9	18	12	238.8 > 194.9	12	0,004	0,010
Piperonyl Butoxide	ESI+	356.1 > 177	18	15	356.1 > 118.9	37	0,0007	0,0025
Pirimicarb	ESI+	239 > 72	20	22	239 > 182	20	0,001	0,003
Pirimiphos Methyl	ESI+	305.8 > 163.9	30	23	305.8 > 107.9	30	0,002	0,005
Tebuconazole	ESI+	308 > 70	32	20	310 > 70	20	0,002	0,005
Tetramethrin	ESI+	332 > 163.9	20	23	332 > 135	18	0,001	0,003
Triticonazole	ESI+	318 > 70	23	18	318 > 124.9	28	0,001	0,004

$^{(*)}$Italics represent degradation products.

(c) Final considerations

The Pampas region has been favourable for agricultural production, with the use of herbicides beginning in the mid-20th century. At first, 2,4-D was primarily used on maize crops, followed by the application of other herbicides such as dicamba, picloram, atrazine, alachlor, trifluralin, metribuzin, and several others. Chemical and mechanical controls were implemented in conjunction during the growing seasons and fallow periods until the 1990s. The early application of 2,4-D substantiates its inclusion in the ANMAT's monitoring protocols to assess drinking water. However, the lack of updated information regarding the current use of pesticides in the country emphasizes the need to take measures to reduce human exposure to these substances.

In the 1990s, the introduction of genetically modified crops and no tillage technology significantly transformed Argentine agriculture. Although these developments led to the emergence of weed populations resistant to herbicides and the use of new herbicide mixtures and/or higher doses, the standards for monitoring drinking water have not kept pace with the incorporation of pesticides in agricultural production. The level of human exposure near agricultural land is contingent upon the distance between households and the closest treated field, the acreage surrounding residences, and the time of year.

This research study revealed the presence of pesticides in water intended for human consumption, which is associated with the production systems in each sampled area. During the 2020-2021 season, corn and soybeans accounted for just under 50% of the cultivated area allocated to summer crops (Fig. 5). The pesticides used in these crops mainly consist of glyphosate, 2,4-D, atrazine, metolachlor, imidacloprid, and chlorpyrifos. Winter crops covered less than 25% of the cultivated area (Fig. 5), with a significant proportion dedicated to fallow. In 2015, a report indicated that during the fallow period in January-December 2013, 41% of the total pesticides regularly used were applied, with

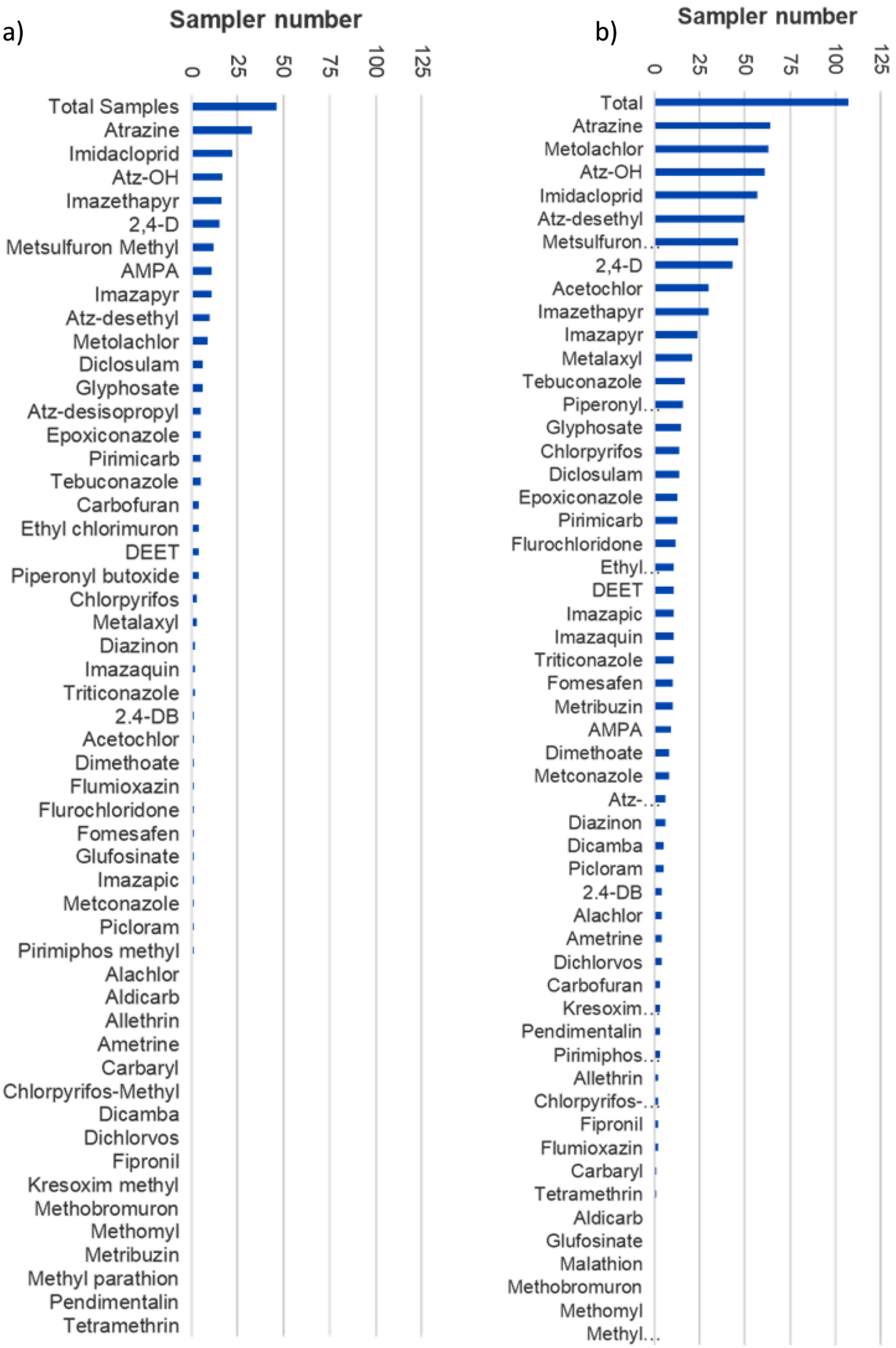

Fig 2. Frequency of pesticides presence in water samples from public supply (a) and private supply (b) in the Pampas region.

36% used in soybeans, 10% in corn, and the remaining 13% in other crops, including winter cereals (Aparicio et al., 2015). Although this trend cannot be directly extrapolated to 2021, the agricultural practices in the area and communications with private consultants suggest that there have been no major changes in input management. The use of pesticides in Argentina has increased between 2000 and 2020 (Palladino et al., 2023), contributing to both rural and urban populations' exposure to diffuse pollution (Fig. 6a). For the first time, this research study analysed 53 pesticides, including some degradation products, in the water. The presence of multiple pesticides in drinking water calls for their immediate inclusion in current regulations for periodic monitoring. People's exposure to pesticides highlights the vulnerability of national public policies that should guarantee the fulfilment of the human right to safe water.

The cumulative presence of pesticide molecules, as depicted in this research study (Fig. 6b), underscores the imperative to enhance agronomic practices aimed at reducing and averting further degradation of drinking water quality. This task should be prioritized in areas where public water supply services are insufficient or non-existent, forcing the population to resort to private supplies. In recent years, the research team has recommended the gradual reduction of pesticide usage, accompanied by responsible agricultural practices that prioritize

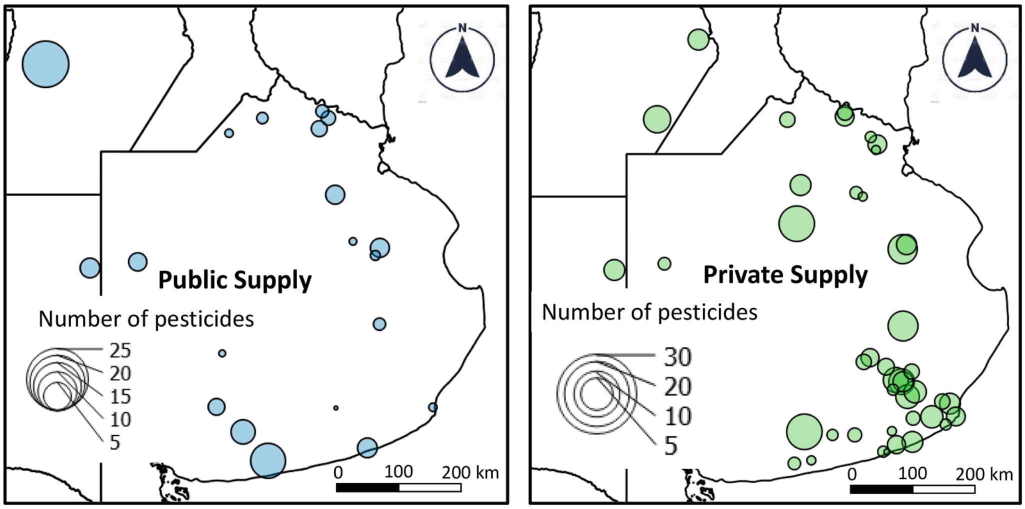

Fig 3. Frequency of pesticides presence in water samples from public supply (blue) and private supply (green) in the Pampas region.

Table 3

Pesticides, the minimum and maximum concentrations in public and private water supplies (stated in µg L^{-1}).

Pesticides	Public Supply		Private Supply		Reference Levels		
	Min.	Max.	Min.	Max.	Argentina Nicolella and de Assis (2022)	Europe Sjerps et al. (2019)	Australia Hamilton et al. (2003)
	µg L^{-1}			µg L^{-1}			
Glyphosate	0,100	0,440	0,182	20,50	-	0.1	10
2,4-D	0,015	1,580	0,015	14,46	100	0.1	0.1
Picloram			0,106	6,700	-	0.1	–
Fomesafen			0,010	5,010	-	0.1	-
Metolachlor			0,002	4,000	-	0.1	2
AMPA	0,167	0,800	0,100	2,600	-	0.1	-
Imazethapyr			0,001	0,775	-	0.1	-
Imazapic			0,241	0,749	-	0.1	-
Imazapyr	0,005	0,145	0,005	0,622	-	0.1	-
Epoxiconazole			0,003	0,585	-	0.1	-
Alachlor			0,008	0,532	-	0.1	-
Imazaquin	0,001	0,175	0,006	0,531	-	0.1	-
Acetochlor			0,012	0,280	-	0.1	-
Tebuconazole			0,001	0,234	-	0.1	-
Atrazine			0,001	0,212	-	0.1	0.5
Metsulfuron Methyl			0,001	0,179	-	0.1	5
Imidacloprid			0,001	0,118	-	0.1	-
DEET			0,010	0,116	-	0.1	-
Atz-desisopropyl			0,006	0,106	-	0.1	-
Tetramethrin			0,106	0,106	-	0.1	-

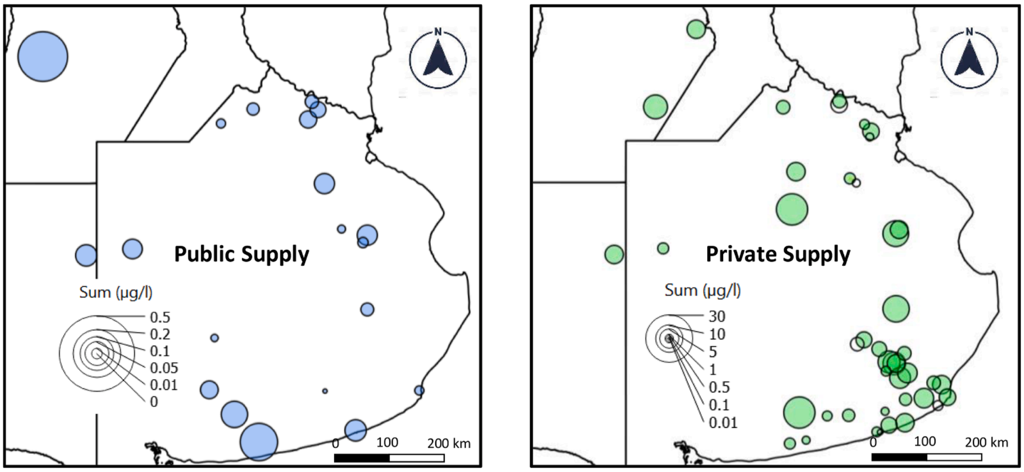

Fig 4. The quantity of pesticides in water samples from public supply (blue) and private supply (green) in the Pampas region.

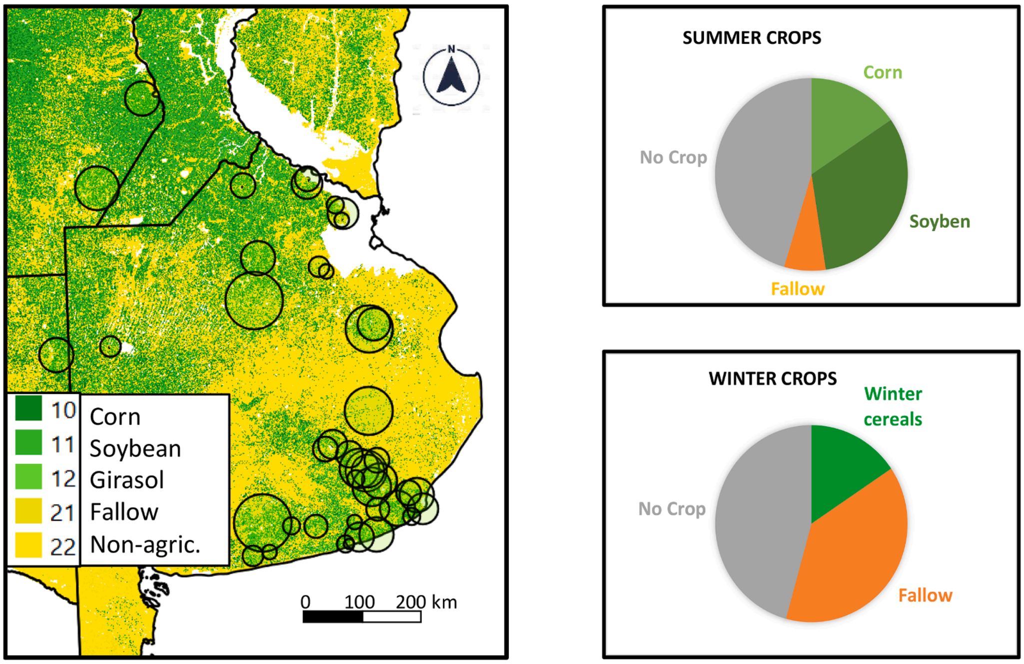

Fig 5. Presence of pesticides in groundwater during the winter (2020) and summer (2020-21) agricultural production in the Pampas region.

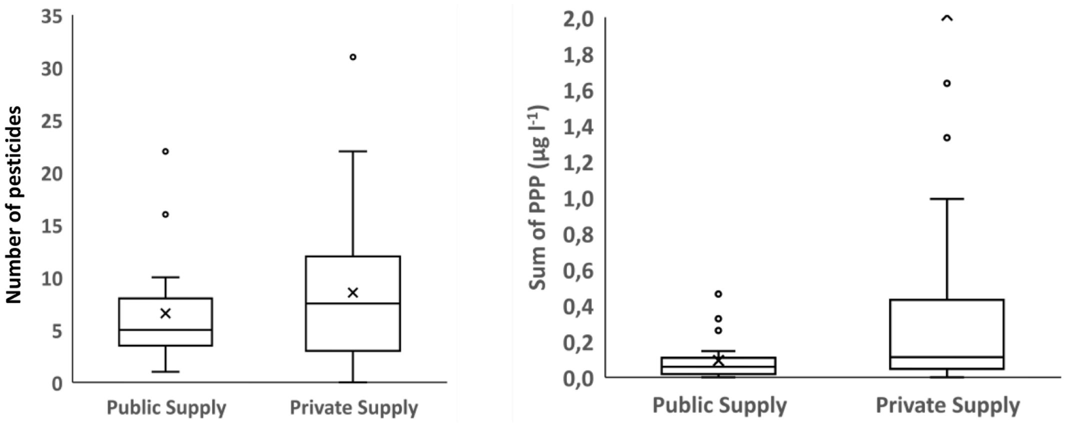

Fig 6. Number of pesticides detected and quantified concentrations in drinking water samples from the Pampas region.

environmental care and community development.

At present, Argentina has a listing of only 18 prohibited pesticides, a number comparable to Uruguay (22), Chile (27), and Paraguay (11) but less than Brazil (133) (PAN, 2023). We noted that in Uruguay, similarly to Argentina, a few active ingredients dominate the market, particularly herbicides, where 88% corresponds to just 5 active ingredients. The market dominance of a few active ingredients makes it easier to include them in drinking water monitoring efforts but could hinder the phase-out of their use. Diminishing pesticide doses requires significant environmental and labour awareness actions, as well as careful control of agricultural practices.

Conclusions

The research study on drinking water in the Pampas region unveils an extensive prevalence of the currently used pesticides.

The individual concentration threshold for pesticides set by the European standards exceeded 8.7% of samples from public supply and 17.6% from private supply. Additionally, the cumulative concentration threshold for pesticides was surpassed in 4.3% of samples from public supply and 13.9% of samples from private supply, according to European standards.

Based on these findings, we strongly recommend incorporating pesticides into the regulations governing the quality control of drinking water and working towards a progressive reduction of pesticide usage in the Argentine agricultural system. These measures will contribute to ensuring the safety and sustainability of drinking water sources for the population.

Considering the evidence presented in Argentina, it is imperative to integrate all available knowledge to establish clear rules for the use and control of pesticides, placing paramount emphasis on global public health.

Environmental implications/effects

This research study analysed pesticides, including some of their degradation products, present in the drinking water within a geographical region characterized by primary agricultural production. These pesticides should be promptly incorporated into current regulations to facilitate their periodic monitoring in water intended for human consumption. Although the presence of pesticides differs among the sources of water for human consumption, diffuse contamination is a reality that affects both rural and urban populations, accentuating the fragility of national public policies tasked with fulfilling the human right to access water in a manner that is sufficient, safe, acceptable and affordable.

CRediT authorship contribution statement

Virginia Aparicio: Conceptualization, Writing – review & editing, Funding acquisition. **Eduardo De Gerónimo:** Methodology, Supervision, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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